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Published in:
Tellus (B)

DOI:
10.1034/j.1600-0889.1999.t01-2-00008.x

Publication date:
1999

Tellus (1999), 51B, 679–687
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TELLUS
ISSN 0280–6509

New early winter f_{CO_2} data reveal continuous uptake of CO_2 by the Weddell Sea

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(Manuscript received 21 January 1998; in final form 15 August 1998)

ABSTRACT

The Antarctic Ocean has been thought to be unimportant for the uptake of CO_2 since upwelling of CO_2-enriched deep waters would favour outgassing. Here we present the first direct f_{CO_2} measurements obtained in early winter under the ice which, combined with estimated entrainment rates, show that the Weddell Sea, an area of intense upwelling manifested by the doming structure of the cyclonic gyre, has the capability to be almost continuously a sink for atmospheric CO_2. A flux, effective after the ice cover disappears, is estimated to be -0.74 ± 0.7 mmol m^{-2} d^{-1}. Combined with a flux estimate in late autumn (-2.0 mmol m^{-2} d^{-1}) integrated over the area of the central Weddell Gyre, a carbon uptake of 0.24×10^{13} gC y^{-1} ($\approx 2.4 \times 10^{-3}$ GtC y^{-1} being $\approx 1‰$ of global uptake) is computed, which is about a third of the strength of the biological pump of the Weddell Sea.

1. Introduction

The Weddell Sea in the Southern Ocean is an area where, due to the prevailing winds, divergent flow leads to significant upwelling. This is obvious from the doming structure of the water mass properties which correlates with a cyclonic gyre circulation (Deacon, 1979). A significant part of the ocean's ventilation takes place due to the formation of Weddell Sea Bottom Water (Reid and Lynn, 1971; Carmack and Foster, 1975; Fahrbach et al., 1994). The newly ventilated water is transported into the Antarctic Circumpolar Current and mixing with adjacent waters results in the final product, the Antarctic Bottom Water, which is traceable to at least the mid latitudes of the northern hemisphere in the Atlantic and Pacific oceans (Mantyla and Reid, 1983). The Weddell Sea is thought to be an important sink for atmospheric CO_2 as suggested by Hoppema et al. (1995). In a later study, Hoppema et al. (1998a) found compelling evidence for anthropogenic carbon uptake in the same area. The high latitude, cold water areas, in combination with their potential physical sink function, are of major interest in the studies of greenhouse gases, especially CO_2 (Poisson and Chen, 1987; Anderson and Jones, 1991). The formation of Antarctic Bottom Water (AABW) in the Weddell Sea brings dissolved CO_2 into the deep ocean thus emphasizing its role in the global carbon budget. Some of the CO_2 uptake may be of anthropogenic origin. However, most of it is a compensation to the outgassing which occurs in equatorial regions (Murray et al., 1995), thus primarily part of the natural, pre-anthropogenic global carbon cycle. Although the problematic increase in atmospheric CO_2 and the role of the global ocean as a sink for atmospheric CO_2 has been debated in detail (Quay

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et al., 1992; Keeling and Shertz, 1993; Siegenthaler and Sarmiento, 1993), it is as yet unclear how large a role the Antarctic Ocean plays in the global climate-related carbon budget, both under natural conditions and when taking into account the recent anthropogenic perturbation (Tans et al., 1990; Sarmiento et al., 1992). Takahashi et al. (1993) presented an overview of available data of the partial pressure of CO_2 for the years 1984–1990 for the Atlantic sector of the Southern Ocean, including the northern Weddell Sea. Generally, undersaturation was observed, albeit in our study area of the Weddell Sea, no data were available due to ice coverage.

The inorganic carbon system in seawater comprises the chemical states HCO_3^-, CO_3^{2-} and $CO_2(aq)$, the latter including a minor amount of H_2CO_3. The system is determined upon measurement of any two of its eight variables. Of those, only four variables are measurable, the fugacity of CO_2 in seawater (f_{CO_2}), the total dissolved inorganic carbon

$$(C_T = [CO_3^{2-}] + [HCO_3^-] + [CO_2(aq)]),$$

pH and total alkalinity. The fugacity of CO_2 (f_{CO_2} in µatm) is the partial pressure pCO_2 (µmol mol^{-1}) after a slight correction (~0.7%) for the non-ideal behaviour of CO_2 in the air/gas mixture (Weiss, 1974). In fact, in seawater there exists the dissolved form $CO_2(aq)$ for which the corresponding f_{CO_2} can be assessed by means of an air/water equilibrator (see below) according to

$$[CO_2(aq)] = \alpha f_{CO_2}, \quad (1)$$

where α is the solubility at a given temperature and salinity (Weiss, 1974). Here we present for the first time accurate direct f_{CO_2} measurements from waters from under the sea ice cover for a nearly zonal transect across the Weddell Sea from Kapp Norvegia to Joinville Island. Earlier, this transect had been investigated (Lemke, 1994; Fahrbach et al., 1994) in other seasons but no direct measurements of f_{CO_2} were performed. Computation of f_{CO_2} from total alkalinity and C_T tends to result in values that are too low (cf. Metzl et al., 1991) and also depend on the carbon dissociation constants (Goyet and Poisson, 1989; Stoll et al., 1993; Roy et al., 1993). Thus, direct measurements are preferred.

2. Sampling and methods

Data are presented from the ANTXIII/4 cruise with R.V. "Polarstern" (Fahrbach, 1997) along a transect across the Weddell Sea occupied in April/May 1996 (Fig. 1). At all hydrographic stations samples were taken using a 24-place rosette sampler equipped with a Conductivity Temperature Depth (CTD) instrument (Falmouth Scientific Instruments, Triton ICTD). Among many other analyses the C_T content was determined for each water sample taken from the rosette sampler. These data are the subject of another paper (Hoppema et al., 1998a) and will not be discussed in detail here.

The f_{CO_2} data were obtained using a fully automated sampling system (designed after Wanninkhof, 1993) including a Li-Cor (LI-COR, Model 6252) infrared analyzer. A continuous supply of marine air was pumped from the crow's nest from which subsamples were taken for determining the mole fraction (mixing ratio) of CO_2 in air (f_{CO_2}). For determination of the f_{CO_2} in seawater, the ship's non-toxic water supply was sprayed at a rate of 40–60 cm^3 s^{-1} into the nozzle of an equilibrator (Bakker et al., 1997; Robertson et al., 1993) with a response time of less than 2 min. Temperature of the inlet system and equilibrator were recorded simultaneously with each measurement. The headspace gas was circulated and subsampled at regular intervals. Atmospheric

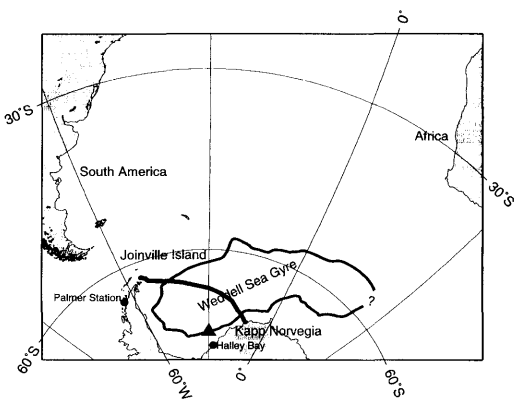

Fig. 1. Map showing the study area. Approximate location of the Weddell Gyre circulation is shown by the thin line, the transect by the bold line and the two NOAA/CMDL air monitoring stations by the big black dots.

pressure in the equilibrator was maintained by means of a bleed valve. A slight modification to the nozzle was made so that ice blockage would hardly occur, thus enabling us to measure waters collected from under the ice. The modified inlet in the hydro-well of R.V. "Polarstern" allowed for a fairly uninterrupted water supply. Samples were dried using Aquasorb (Merck) before being flushed through the IR cell.

The reference gases were calibrated against National Oceanic and Atmospheric Administration (NOAA) certified standard gas mixtures (accurate to ± 0.01 μmol mol^{-1}), before and after the cruise. For all reference gases the precision during the calibration was better than 0.07 μmol mol^{-1}. No significant difference could be observed between the pre-cruise and post-cruise calibrations. A typical analysis cycle (which takes less than one hour) consists of a calibration (using three reference gases of 266.95, 367.76 and 443.66 μmol mol^{-1} CO_2 in air), air, seawater (5×), air, seawater (5×) and a calibration. For each sample 10 readings (0.5 s) were taken and averaged during post-processing. Final data were obtained by interpolating between two consecutive calibration cycles.

Due to the transport of the water from inlet to equilibrator a slight heating occurred, which was generally less than 0.1°C and reached maximum values of 0.3–0.4°C. Data with a temperature difference that was too large (indicative of blockage in the water supply) and typical outliers were discarded. Sometimes foam formation occurred within the equilibrator, probably due to the presence of organic matter, thus giving erroneous, spiky f_{CO_2} readings. This occurred primarily in the middle part of the transect. These data were also discarded. The remaining data set totals over 2300 data points. For the flux computations, the shipboard meteorological data were used with the assumption of 100% atmospheric moisture content at the sea surface.

The lack of f_{CO_2} data for the middle part of the transect is rather unfortunate but can be remedied by interpolating data using the surface C_T data (Hoppema et al., 1998a) normalized to a salinity of 35 and an assumed conservative, normalized total alkalinity in the Weddell Sea (Poisson and Chen, 1987; Anderson et al., 1991). The latter includes minor corrections for nutrient contributions. For this computation we used the dissociation constants determined by Roy et al. (1993). Using the surface water value for C_T ($S=35$) from Hoppema et al. (1998a) in combination with our f_{CO_2} data (342 ± 3 μatm) we computed a normalized total alkalinity of 2380 ± 12 μeq kg^{-1} (Table 1). The obtained value is close to that reported by Anderson et al. (1991) and Millero et al. (1998) for the Weddell Sea, lending support to the accuracy of our measurements, as well as to the validity of our approach. Salinity data from the thermosalinograph were interpolated on the basis of the surface bottle data obtained from the rosette sampler.

Table 1. *Total alkalinity (in μeq kg^{-1}) and C_T (in μmol kg^{-1}) normalized to a salinity of 35 for the surface water (SW) and the Warm Deep Water (WDW); values taken from Hoppema et al. (1998a); the calculated value for total alkalinity is underlined*

	Total alkalinity	C_T
SW	2387	2252.5
WDW	<u>2380</u>	2286

3. Results

Fig. 2 shows the online salinity data plotted versus longitude. Over the entire transect the salinity in the near surface layer ranged between 33.85 to 34.45. In the east and the center of the

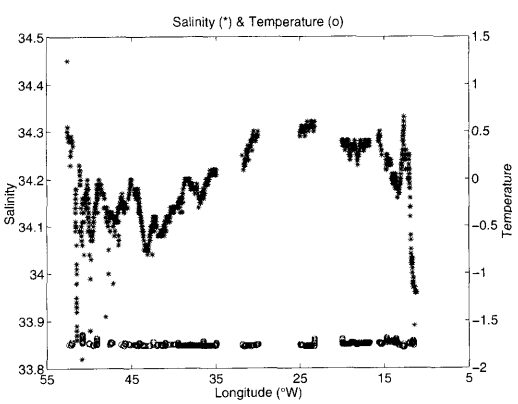

Fig. 2. Plot of salinity (stars) /temperature (circles) versus longitudinal position from Kapp Norvegia (right side) to Joinville Island (left side).

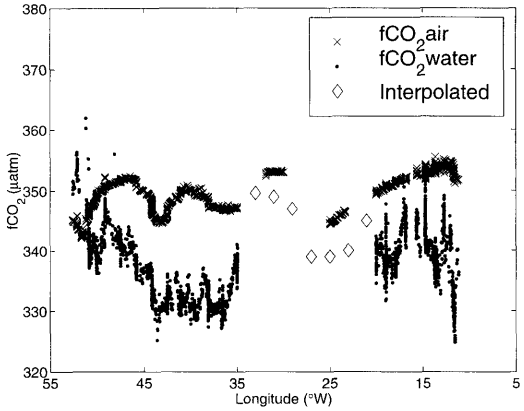

Fig. 3. Plot of f_{CO_2} in air (crosses) and f_{CO_2} in the fully ice-covered surface water (small diamonds) versus longitudinal position from Kapp Norvegia (right side) to Joinville Island (left side). Interpolated f_{CO_2} data (derived from C_T and total alkalinity) are shown by the large diamonds (see text for explanation).

section, the values are generally higher than in the west. Close to the coastline, both in the east and in the west, the variability is large. Differences in salinity reflect the different stages of formation of the winter mixed layer. Temperature remained approximately constant with values close to the freezing point.

The f_{CO_2} data versus longitude are shown in Fig. 3. Due to atmospheric pressure changes the f_{CO_2} in air fluctuates which is clearly seen in Fig. 3. The eastern part of the transect shows the f_{CO_2} in water to be undersaturated, relatively to the f_{CO_2} in air. Near the center (around 35°W) the values are closer to equilibrium values (based on the actual measured values and the interpolated ones) which might be attributed to local upwelling of CO_2-rich Warm Deep Water (WDW). Further west the surface water f_{CO_2} again is generally undersaturated. A striking feature is the transition in the western part of the gyre from undersaturation to supersaturation. The supersaturation reaches a local maximum close to Joinville Island.

4. Discussion

Long-term measurements of f_{CO_2} in air (Conway et al., 1994) show a general increasing trend to the north in the Atlantic sector. Extrapolation of the f_{CO_2} time series of two stations in the vicinity of our transect (Halley Bay and Palmer Station; for station positions see Fig. 1) was performed for the months April/May 1996, the time period of our cruise. Our mole fractions of CO_2 in air vary from ~ 360.5 µmol mol^{-1} in the western end of the transect to values of ~ 361.5 µmol mol^{-1} in the eastern part. These values are higher by only ~ 0.3–0.6 µmol mol^{-1} compared to the extrapolated values of Halley Bay (361.27 µmol mol^{-1}) and Palmer station (359.92 µmol mol^{-1}).

The occasional spiky f_{CO_2} readings in the center part of the transect may be due to either organic matter or algae in the water supply (Fig. 3). The resultant foam formation gives rise to high fluctuations in the readings taken from the infrared analyzer. The most likely cause for foam formation is dissolved organic matter rather than intact algal material. Samples taken for Chlorophyll *a* (Chl*a*) content in the surface water showed low values (of the order of ~ 0.1–0.2 µg dm^{-3}) (C. Dubischar, AWI, personal communication, 1997), too low to explain the observed phenomenon, thus we decided to exclude all those data from our interpretation.

Strong cooling during fall appears to be the driving force for the observed undersaturation in f_{CO_2} in the surface water. This rapid process prevents total equilibration of the surface mixed layer with the atmosphere, which thus has a deficit in CO_2 content. During winter, the ice cover seriously restricts gas exchange, again preventing equilibration with the atmosphere (Chen, 1982; Schlosser et al., 1987). The observed increase in f_{CO_2} (e.g. the central part of the transect; Fig. 3) can only then occur due to entrainment of Warm Deep Water ($T > 0.2$°C) with its high C_T and f_{CO_2} (Poisson and Chen, 1987; Hoppema et al., 1995). The CO_2 increase could also be due to in situ mineralization of organic matter. For example, this might have occurred in the western part of the transect (Fig. 3), but eludes definite explanation. It might also be a remnant signal of previous years as the water is advected from the south, where it circulates under the perennial ice cover thus not coming into contact with the atmosphere for more than one year (Weppernig et al., 1996).

The instantaneous gas exchange flux across the air-sea interface is given by the equation

$$F = k\Delta f_{CO_2} \qquad (2)$$

in which k is the gas transfer coefficient, which is a function of the wind speed, salinity and temperature, including chemical enhancement (Wanninkhof, 1992) and Δf_{CO_2}, the gradient of the fugacity of CO_2 between the atmosphere and the sea surface. During the time when the sea ice cover is developing, the wind cannot have a direct effect on the calculated flux. The gas exchange being restricted severely, the flux is then determined by the chemical enhancement factor and Δf_{CO_2}. We define this scenario as the potential flux. After break-up of the ice cover an almost instantaneous exchange can take place, the size depending of course on the determined gradient of f_{CO_2} between atmosphere and ocean and for a very large part on the wind speed.

Using a windspeed of $\sim 0\ m\ s^{-1}$ (due to ice cover) we find a potential flux of -0.96 mmol $m^{-2}\ d^{-1}$ as an average over 2075 km of the transect. This figure appears to be close to the values of Bakker et al. (1997) (-1.0 to -1.2 mmol $m^{-2}\ d^{-1}$; mean windspeed) for the eastern part of the Weddell Sea, albeit the latter were averaged over an area between 47–60°S. We would like to stress the fact that this is a potential flux estimate at the beginning of the winter period. Due to the ice cover, the air-sea gas exchange is almost completely absent (Schlosser et al., 1987). During the ensuing winter period, the f_{CO_2} of the surface layer increases due to the entrainment of Warm Deep Water with a high f_{CO_2}. Due to tidal movement the ice pack is not completely closed off. However we regard this effect to have a negligible influence, based on the visual sightings which showed total coverage of the study area.

The key question in determining whether the Weddell Gyre is a source or a sink for CO_2 is how much the surface water is diluted by entrainment of Warm Deep Water. During the ice-free season, wind stirring and heat loss to the atmosphere occur, but result in a negligible amount of entrainment (Gordon and Huber, 1990). These authors concluded that entrainment occurs during the winter period when the ice covers the sea surface. Different entrainment rates are reported in literature (Gordon and Huber, 1990; Schlosser et al., 1987; Hoppema et al., 1998b). Hoppema et al. (1998b) computed a lower rate (35 m y^{-1}) for the central Weddell Gyre as compared to the rate obtained (45 m y^{-1}) by Gordon and Huber (1990) for the area near Maud Rise. Both based their values on the assumption that upwelling is negligible during periods without ice cover. Hoppema et al. (1998b) based their calculation on data obtained from two cruises in the same area, whereas Gordon and Huber (1990) used data from a single cruise and based their estimate on an assumed oxygen value, to which the computation is rather sensitive. We therefore assume the rate from Hoppema et al. (1998b) to be more accurate.

Applying an entrainment rate of 35 m y^{-1} we compute the change in C_T in the surface layer during the winter period. Using our total alkalinity (Table 1) we compute an f_{CO_2} level of 360 ± 4 µmol mol^{-1} at the end of winter when the sea ice melts. This value is equal to the mean value of the f_{CO_2} in the atmosphere (361 ± 0.7 µmol mol^{-1}). If we assume a typical winter mixed layer depth of 100 m, we can estimate the C_T of surface water for spring conditions as follows:

$$(1 - F)[\mathrm{SW}] + C[\mathrm{WDW}] = [\mathrm{SW}_{\mathrm{spring}}], \qquad (3)$$

where F is the fraction of WDW entrained into the surface layer. [SW] and [WDW] are the C_T concentrations in the surface water (SW) and WDW, respectively, and $[\mathrm{SW}_{\mathrm{spring}}]$ is the estimated value at the end of the winter period. For a 7-month period the fraction F would be $7/12 \times 35 = 20\%$, using a winter mixed layer depth of 100 m. Our results show that the f_{CO_2} of the Weddell Sea after a 7-month period of ice coverage (Anonymous, 1985) is on average close to equilibrium with the atmosphere. During the onset of spring the water temperature will rise with a related increase in f_{CO_2} at constant $[CO_2(aq)]$ due to a decrease in α in eq. (1) above. This increase would thus be able to actually result in a flux of CO_2 from the ocean to the atmosphere. On the other hand, the onset of phytoplankton growth has ample potential to offset this effect (Hoppema et al., 1995). In fact, the ensuing bloom of phytoplankton in spring will result in an immediate uptake of CO_2 thus ensuring a prolonged undersaturation (Bakker et al., 1997). As soon as the sea ice cover opens up, the flux will also be increased by the windspeed which is estimated to be in the range of 6.0–8.6 m s^{-1} (European Center for Medium-Range Weather Forecasting; monthly averages).

Disregarding the possible effect of phytoplankton growth on CO_2 uptake (which would create undersaturation) we can compute a strictly

physically mediated flux. Taking a mean windspeed of 7.3 m s^{-1} we compute a mean flux of -0.74 ± 0.7 mmol m^{-2} d^{-1} for the transect. This flux should be considered as a lower estimate since the effect of phytoplankton growth has not been taken into account. Although a relatively small number, the flux indicates uptake by the ocean, even after a 7-month time period during which no gas exchange could take place and during which the CO_2 content in the water was increased by entrainment only. This flux can be integrated over an area of 0.8×10^6 km^2, representing the central Weddell Gyre, over a 10 day period in which the sea ice cover will further break up. Due to the subsequent warming of the surface waters f_{CO_2} would increase, if it were not for the phytoplankton blooms with their rapid consumption of CO_2 resulting in further undersaturation. Clearly the central Weddell Gyre, being undersaturated in CO_2 for the larger part of the year, is an important region for CO_2 uptake (Anderson and Jones, 1991). In order to arrive at an annual estimate for carbon uptake (excluding the effect of biology) we include the "conditioning" period in autumn, where due to the rapid cooling over about 45 days, a strong undersaturation is created. For this estimate we use the surface water value we measured under the ice. Again computing the flux (with a monthly averaged windspeed of 6 m s^{-1}) we obtain a value of -2.0 mmol m^{-2} d^{-1}. This value is larger than the flux calculated at the end of the winter since the undersaturation at that time was much smaller. Adding these two numbers over their relevant time periods and integrating over the above mentioned surface area of the Weddell Gyre we obtain a carbon uptake rate of 0.24×10^{13} gC y^{-1} ($\approx 2.4 \times 10^{-3}$ GtC y^{-1}). This value is the physically induced uptake rate for the Weddell Gyre. Since we have neglected any effect of phytoplankton growth induced f_{CO_2} undersaturation, it is a lower limit. To incorporate a tentative value for phytoplankton induced CO_2 uptake would be beyond the scope of this paper.

The value obtained is approximately 30% of the value (0.8×10^{13} gC y^{-1}) obtained by Hoppema et al. (1998b) in which a budget approach was used for the same study area. The CO_2 uptake estimated in the present study is completely physically mediated, whereas the estimate by Hoppema et al. (1998b) is largely determined by biological processes (the biological carbon pump; Volk and Hoffert, 1985). Hence the total CO_2 uptake in the Weddell Sea being the sum of above two estimates amounts to about 1.04×10^{13} gC y^{-1} (~ 0.01 GtC y^{-1}).

In this deep water formation area, the ratio between physical and biological pump thus appears to be of the order of 1 : 3. The biological pump works 3 times more effectively than the physical pump. A comparison with another important deep water formation area, the North Atlantic (Stoll et al., 1996) shows that in this area the ratio between physical pump and the biological pump also equals 1 : 3. In contrast to the Antarctic which can be described as a High Nutrient/Low Chlorophyll area (Chisholm and Morel, 1991) and a low productivity area (El-Sayed, 1984), the North Atlantic has lower nutrient availability (relative to the Antarctic) but higher chlorophyll *a* biomass.

The uptake of CO_2 by surface water would eventually lead to saturation if no subsequent transport, either vertically or horizontally would take place. The formation of Weddell Sea Bottom Water through mixing of Warm Deep Water with the dense shelf water is one pathway by which CO_2 is transported into the deep ocean (Anderson et al., 1991). This holds also true for some deep water formation (Orsi et al., 1993). Another large part of the surface water is removed from the Weddell Sea through northward Ekman transport (Levitus, 1988).

Our conclusion that the Weddell Sea is a sink for atmospheric carbon dioxide is based on an extrapolation of early winter data in combination with an accurate estimate of entrainment rate of deep water into the surface water. Several authors suggest that during the spring/summer season the Southern Ocean is at or near equilibrium with the atmosphere (Murphy et al., 1991a,b; Metzl et al., 1991; Poisson et al., 1994). On the contrary Takahashi et al. (1993) found the Southern Ocean to be a sink in our study region as was also suggested by model studies (Tans et al., 1990, Louanchi et al. 1999). The work done by Robertson and Watson (1995) also showed the south Atlantic area to be a sink for atmospheric CO_2.

Although there appears to be more and more evidence that the Southern Ocean is indeed a sink, albeit a modest one, there is still controversy as

to its magnitude in the global carbon budget. Anderson and Jones (1991) estimated a maximum of anthropogenic CO_2 sequestration of 24×10^{12} gC y^{-1} (≈ 0.024 GtC y^{-1}) in the Weddell Sea. However, this value is not directly comparable with our estimate of the annual uptake. Anderson and Jones (1991) mentioned that biological production might significantly enhance CO_2 sequestration. Robertson and Watson (1995) used interpolated data between two cruises on either side of our study area and came to a sink function of 0.07 to 0.10 GtC for 4 summer months of which they deemed 0.10 GtC to be more realistic. Their number should be divided by ~ 9 since they used a surface area of 9×10^6 km^2, thus coming to a number of ~ 0.01 GtC per 4 months. Although there was no clear correlation between the measured f_{CO_2} and phytoplankton abundance they suggested that the observed undersaturations were caused by biological activity which had occurred earlier in the season. The lack of winter/autumn data prevented the extrapolation to an annual uptake rate, but in all likelihood this would be a rather small adjustment.

In fact, during the autumn/winter there will be only a physical mediated uptake, which we calculated to be 2.4×10^{-3} GtC y^{-1}. Adding both these estimates we obtain to ~ 0.012 GtC y^{-1}, very close to the estimate by Hoppema et al. (1998b) (~ 0.01 GtC y^{-1}). In recent modelling work Chen (1997) estimated the ice-covered area of the Weddell Sea to have a physical induced uptake rate of 0.01 GtC y^{-1}, increasing to 0.04 GtC y^{-1} when incorporating the contribution of biological processes. Our value appears to be in the lower range but merely illustrates the need for improved understanding of the physical/biological processes which control the gas exchange in the surface ocean. Direct measurement of f_{CO_2} are superior to derived values of f_{CO_2} as calculated from total alkalinity and C_T. High quality measurements of the carbonate system combined with phytoplankton abundance in detailed spatio-temporal sense should be continued in this area where upwelling and deep water formation play a major rôle in uptake of carbon dioxide next to the fact that biological fixation might play an even larger role.

5. Acknowledgements

This research was part of the Netherlands JGOFS program and was supported by VvA9, subsidiary of the Netherlands Organisation for Scientific Research (NWO) and the "Forschungs- und Entwicklungsvertrag Zusammenarbeit zwischen AWI und NIOZ", project: "Austausch von Kohlendioxid zwischen Südpolarmeer und der Atmosphäre". We are indebted to the captain, officers and crew of R. V. "Polarstern" for their pleasant co-operation during the cruise. The comments of two anonymous reviewers helped to improve the original version of the manuscript. This is NIOZ publication number 3156 and AWI-contribution number 1273.

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